Palladium-catalyzed formal hydroacylation of allenes employing carboxylic anhydrides and hydrosilanes

Tetsuaki Fujihara*, Takuro Hosomi, Cong Cong, Tomoya Hosoki, Jun Terao and Yasushi Tsuji*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan.

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Allene
Carboxylic anhydride
Hydroacylation
Hydrosilane
Palladium

ABSTRACT

The formal hydroacylation reaction of allenes has been developed employing carboxylic anhydrides as acyl sources and hydrosilanes as reducing reagents in the presence of a commercially available palladium complex as a catalyst. The reaction affords α,β-unsaturated ketones regio- and stereoselectively. The similar catalyst system is also effective for the reduction of carboxylic anhydrides to the corresponding aldehydes employing hydrosilanes.

1. Introduction

Hydroacylation reaction involving the addition of aldehydes to carbon-carbon multiple bonds is a useful synthetic method to provide unsymmetrical ketones atom-economically.[1] However, intermolecular hydroacylation of alkenes and alkynes often suffers from low selectivity and low yields. In order to ensure high efficiency, i) intramolecular reaction,[2] ii) substrates bearing suitable directing groups,[3] and/or iii) carbon monoxide pressure,[4] were often indispensable. An alternative method is a formal hydroacylation employing a suitable acyl source in place of an aldehyde. The oxidative or reductive formal hydroacylation employing alcohols as acyl donors were reported.[5] We recently found the palladium-catalyzed formal hydroacylation of allenes employing acid chlorides and hydrosilanes.[6] The reaction afforded the corresponding α,β-unsaturated ketones regio- and stereoselectively.

Carboxylic anhydrides are stable, easy-to-handled, and easy-to-prepare compounds from the corresponding carboxylic acids, and are one of the most useful compounds in organic synthesis. Regarding the transition-metal catalyzed reactions, it is known that the oxidative addition of the C(acyl)-O bond proceeds in the presence of suitable transition-metal complexes.[7] Thus, carboxylic anhydrides were used as an acyl source in the palladium-catalyzed cross-coupling reactions employing organoboronic acids[8] and organozinc reagents.[9] Carboxylic anhydrides were also utilized in the formal hydroacylation of styrene derivatives in the presence of a rhodium catalyst.[10] However, a burnable hydrogen gas was used as a reducing agent.

Herein, we report the palladium-catalyzed formal hydroacylation of allenes employing carboxylic anhydrides with stable and easy-to-handle hydrosilanes as a reducing agent. As for the hydroacylation of allenes using aldehydes,[11] there have been only two precedents to date, in which the aldehydes must bear hydroxyl[11a] or thioether[11b] functionalities as directing groups. Noteworthy is that no directing groups are necessary in the present reaction.

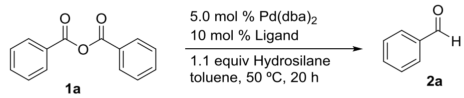
2. Palladium-catalyzed reduction of carboxylic anhydrides

Before investigating the formal hydroacylation of allenes, we carried out reduction of carboxylic anhydrides to aldehydes employing hydrosilanes as a reducing agent. Yamamoto and co-workers carried out the reduction of carboxylic anhydrides to the corresponding aldehydes in the presence of palladium catalysts.[12] However, the reaction required high pressure (3.0 MPa) of molecular hydrogen. Based on our previous report that a palladium complex efficiently catalyzes the reduction of carboxylic acids in the presence of pivalic anhydride,[13] Pd-catalyzed reduction of carboxylic anhydrides employing hydrosilanes to the corresponding aldehydes was carried out. Thus, benzoyl anhydride (**1a**) was treated with a mixture of $Pd(dba)_2$ and $P(p\text{-}MeOC_6H_4)_3$ as a catalyst in the presence of

* Corresponding author. Tel.: +81-75-383-2515; fax: +81-75-383-2514; e-mail: ytsuji@scl.kyoto-u.ac.jp

* Corresponding author. Tel.: +81-75-383-2517; fax: +81-75-383-2514; e-mail: tfuji@scl.kyoto-u.ac.jp

Table 1
Effect of ligands and hydrosilanes on the palladium-catalyzed reduction of benzoic anhydride (**1a**)[a]

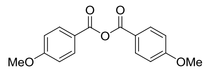
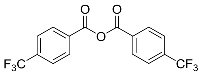
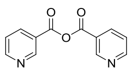
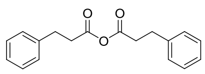
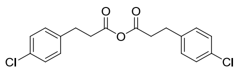
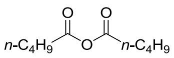
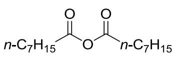
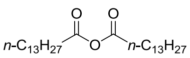
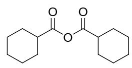


1a **2a**

Entry	Ligand	Hydrosilane	Yield (%)[b]
1	P(p-MeOC$_6$H$_4$)$_3$	H$_2$SiMePh	85
2	none	H$_2$SiMePh	trace
3	PPh$_3$	H$_2$SiMePh	68
4	P(p-MeC$_6$H$_4$)$_3$	H$_2$SiMePh	74
5	PCy$_3$	H$_2$SiMePh	66
6	P(p-MeOC$_6$H$_4$)$_3$	HSiEt$_3$	67
7	P(p-MeOC$_6$H$_4$)$_3$	HSi^{i}Pr$_3$	14
8	P(p-MeOC$_6$H$_4$)$_3$	H$_2$SiEt$_2$	74
9	P(p-MeOC$_6$H$_4$)$_3$	H$_2$SiPh$_2$	9
10[c]	P(p-MeOC$_6$H$_4$)$_3$	H$_2$SiMePh	81

[a] Reaction conditions: benzoic anhydride (**1a**: 0.50 mmol), hydrosilane (0.55 mmol), Pd(dba)$_2$ (0.025 mmol, 5.0 mol %), ligand (0.05 mmol, 10 mol %, P/Pd = 2) in toluene (1.0 mL) at 50 °C for 20 h. [b] Yield based on the GC internal standard technique. [c] MeCN (1.0 mL) was used as the solvent.

Table 2
The palladium-catalyzed reduction of carboxylic anhydrides to the corresponding aldehydes[a]

Entry	Carboxylic anhydride (**1**)	Temp. (°C)	Yield (%)[b]
1	 **1b**	50	**2b**: 83
2[c]	 **1c**	40	**2c**: 52
3	 **1d**	40	**2d**: 75
4	 **1e**	60	**2e**: 76
5	 **1f**	40	**2f**: 70
6	 **1g**	50	**2g**: 88[d]
7	 **1h**	50	**2h**: 93[d]
8	 **1i**	60	**2i**: 82
9	 **1j**	120	**2j**: 73[d]

[a] Reaction conditions: carboxylic anhydride (**1**: 0.50 mmol), H$_2$SiMePh (0.55 mmol), Pd(dba)$_2$ (0.025 mmol, 5.0 mol %), P(p-MeOC$_6$H$_4$)$_3$ (0.050 mmol, 10 mol %, P/Pd = 2) in toluene (1.0 mL), for 20 h. [b] Isolated yield. [c] Pd(dba)$_2$ (0.05 mmol, 10 mol %), P(p-MeOC$_6$H$_4$)$_3$ (0.10 mmol, 20 mol %, P/Pd = 2). [d] Yield based on the GC internal standard technique.

H$_2$SiMePh as a reducing agent in toluene at 50 °C (Table 1). As a result, benzaldehyde (**2a**) was obtained in 85% yield (entry 1). Without the ligand, **1a** did not convert at all (entry 2). As the ligand, PPh$_3$, P(p-MeC$_6$H$_4$)$_3$ and PCy$_3$ also afforded **2a** in good yields (entries 3–5). As for hydrosilanes, HSiEt$_3$ afforded **2a** in 67% yield, while more bulky HSi^{i}Pr$_3$ was not efficient (entries 6 and 7). H$_2$SiEt$_2$ and H$_2$SiPh$_2$ provided **2a** in 74% and 9% yields, respectively (entries 8 and 9). MeCN was also a good solvent in the reaction (entry 10).

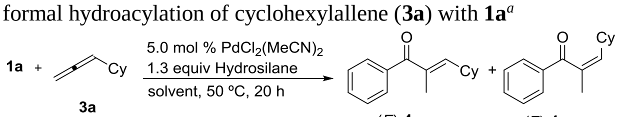
Various carboxylic anhydrides were smoothly converted to the corresponding aldehydes in good to high yields (Table 2). Among them, the reaction of an aromatic acid anhydride having an electron donating group (-OMe) proceeded smoothly, giving the corresponding aldehyde in 83% yield (entry 1). In the reaction of **1c** bearing an electron withdrawing group (-CF$_3$), **2c** was isolated in 52% yield (entry 2). 3-Pyridinecarboxylic anhydride **1d** gave **2d** in good yield (entry 3). With 3-arylpropionic acid anhydrides (**1e** and **1f**), the desired aldehydes (**2e** and **2f**) were obtained in good yields (entries 4–5). Other aliphatic acid anhydrides such as **1g**, **1h**, and **1i** also converted to the corresponding aldehydes in 88%, 93%, and 82% yields, respectively (entries 6–8). In addition, cyclohexanecarboxylic anhydride **1j** also afforded **2j** in 73% yield by elevating the reaction temperature to 120 °C (entry 9). Unfortunately, pivalic anhydride could not be employed as the substrate in the present catalytic system possibly because of its steric hindrance.

3. Palladium-catalyzed formal hydroacylation of allenes

As mentioned above, a hydrosilane is an excellent reducing reagent for the reduction of carboxylic anhydrides. Thus, the formal hydroacylation of cyclohexylallene (**3a**) with **1a** was carried out using HSi^{i}Pr$_3$ as a reducing agent in the presence of a catalytic amount of PdCl$_2$(MeCN)$_2$ in MeCN at 50 °C (Table 3). Under the reaction conditions, an E/Z mixture of hydroacylated product (**4a**) was obtained in 96% total yield with good E-selectivity (E/Z = 88/12, entry 1). By column chromatography, pure (E)-**4a** was isolated in 71% yield. In this reaction, the addition of auxiliary ligands such as PPh$_3$ inhibited the formation of **4a** (entry 2). As for hydrosilane, HSiEt$_3$, HSiPh$_3$ and HSi(OEt)$_3$ were not effective (entries 3–5). PhCN as a solvent provided **4a** in 72%, while DMF and THF were not suitable for this reaction (entries 6–8).

Next, the formal hydroacylation of several allenes (**3**) with carboxylic anhydrides (**1**) was carried out under the same reaction conditions as in entry 1, Table 3 (Table 4). The reaction

Table 3
Optimization of reaction conditions on the palladium-catalyzed formal hydroacylation of cyclohexylallene (**3a**) with **1a**[a]

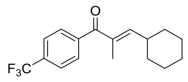
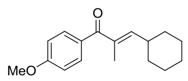
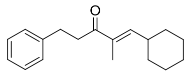
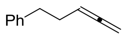
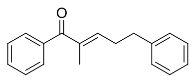
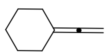
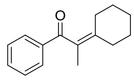


3a (E)-**4a** (Z)-**4a**

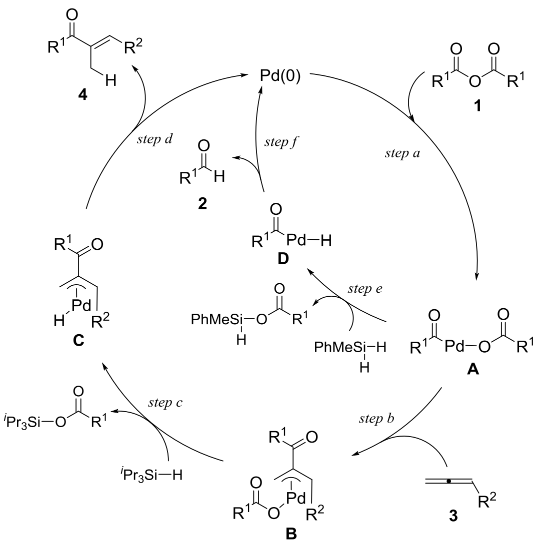
Entry	Hydrosilane	Solvent	Total yield (**4a**) (%)[b]	Selectivity (E/Z)[c]
1	HSi^{i}Pr$_3$	MeCN	96 (71)[d]	88/12
2[e]	HSi^{i}Pr$_3$	MeCN	0	--
3	HSiEt$_3$	MeCN	37	88/12
4	HSiPh$_3$	MeCN	20	86/14
5	HSi(OEt)$_3$	MeCN	39	78/22
6	HSi^{i}Pr$_3$	PhCN	81	89/11
7	HSi^{i}Pr$_3$	DMF	29	86/14
8	HSi^{i}Pr$_3$	THF	7	--

[a] Reaction conditions: **1a** (0.50 mmol), cyclohexylallene (**3a**: 1.0 mmol), hydrosilane (0.65 mmol), PdCl$_2$(MeCN)$_2$ (0.025 mmol, 5.0 mol %), solvent (1.0 mL) at 50 °C for 20 h. [b] Based on the GC internal standard technique. [c] Determined by GC and GC-MS analysis. [d] Isolated yield of (E)-**4a**. [e] PPh$_3$ (0.050 mol) was added.

Table 4
The palladium-catalyzed formal hydroacylation of allenes[a]

Entry	Carboxylic anhydride (**1**)	Allene (**3**)	Yield of (*E*)-**4** (%)[b] (*E*/*Z* ratio in crude)[c]
1	**1c**	**3a**	 **4b**: 81 (93/7)
2	**1b**	**3a**	 **4c**: 41 (84/16)
3[d]	**1e**	**3a**	 **4d**: 81 (94/6)
4	**1a**	 **3b**	 **4e**: 40 (91/9)
5	**1a**	 **3c**	 **4f**: 73

[a] Reaction conditions: anhydride (**1**, 0.50 mmol), allene (**3**, 1.0 mmol), triisopropylsilane (0.65 mmol), $PdCl_2(MeCN)_2$ (0.025 mmol, 5.0 mol %), MeCN (1.0 mL) at 50 ºC for 20 h. [b] Isolate yield of (*E*)-**4**. [c] *E*/*Z* ratio of crude reaction mixture by GC and GC-MS analysis. [d] 10 mol % catalyst was used.



Scheme 1. Proposed mechanism.

of **3a** with an aromatic carboxylic anhydride bearing electron withdrawing groups ($-CF_3$) gave (*E*)-**4b** in high yield (entry 1). On the other hand, an aromatic carboxylic anhydride with electron donating groups (-OMe) afforded the α,β-unsaturated ketones (**4c**) in moderate yield with lower *E*/*Z* selectivity (entry 2). The reaction of 3-phenylpropionic anhydride (**1e**) gave the corresponding product (**4d**) in 81% yield in the presence of 10 mol % palladium catalyst (entry 3). The reaction of 1-(2-phenylethyl)allene (**3b**) with **1a** afforded the corresponding α,β-unsaturated ketone (*E*)-**4e** in 40% yield (entry 4). Gratifyingly, 1,1-disubstituted allene (**3c**) also provided the desired product (**4f**) in good yield (entry 5). Unfortunately, the formal hydroacylation of 1-phenylallene only afforded the corresponding product in poor yields.

As for reaction mechanism, the reduction of **1** employing hydrosilanes would share several catalytic steps with the formal hydroacylation of **3** with **1** (Scheme 1). The oxidative addition of the Pd(0) active catalyst species to a carbon-oxygen bond of **1** affords an acyl palladium species **A** (step a).[14] In the formal hydroacylation of **3**, the insertion of **3** to the palladium-carbon bond of **A** gives an allyl palladium intermediate **B** (step b). Then, reaction of **B** with hydrosilane affords an allylhydrido intermediate **C** (step c). Finally, the reductive elimination affords α,β-unsaturated ketone (**4**) as the product, and the Pd(0) catalyst species regenerates (step d). In the reduction of **1**, **A** reacts with hydrosilane directly, giving an acylhydrido intermediate **D** (step e). The reductive elimination of **D** affords aldehyde (**2**) as the product and the Pd(0) species regenerates (step f).

4. Conclusions

We found that hydrosilanes are versatile reducing reagents in the formal hydroacylation reaction of allenes using carboxylic anhydrides as an acyl source in the presence of a commercially available palladium complex as a catalyst. The reactions afforded α,β-unsaturated ketones regio- and stereoselectively. In the presence of the similar catalyst system, the reduction of carboxylic anhydrides to the corresponding aldehydes proceeded effectively.

5. Experimental section

5.1. General

All manipulations were performed under an argon atmosphere using standard Schlenk-type glassware on a dual-manifold Schlenk line. Solvents were dried and purified before use by usual methods.[15] ^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). GC analysis was carried out using Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-1, 0.25 mm i.d. × 25 m). Medium-pressure column chromatography (MPLC) was performed with a Biotage IsoleraOne (SNAP Ultra 25g). Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63-210 µm). TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F254. Unless otherwise noted, materials obtained from the commercial suppliers were used without further purification.

5.2. General procedure for the palladium-catalyzed reduction of carboxylic anhydrides (Table 1 and Table 2)

To a 10 mL Schlenk flask with a magnetic stir bar, a carboxylic anhydride (**1**, 0.50 mmol), $Pd(dba)_2$ (0.025 mmol) and $P(p\text{-}OMeC_6H_4)_3$ (0.050 mmol) were added. The flask was evacuated and backfilled with argon three times. Then, toluene (1.0 mL) was added to the flask and the resultant solution was stirred at room temperature for 10 min. After $H_2SiMePh$ (0.55 mmol) was added to the flask, the reaction mixture was stirred at 40–120 °C for 20 h under an argon atmosphere. The reaction mixture was cooled to room temperature, the yield of aldehyde (**2**) was determined by GC analysis or the product was isolated with silica gel column chromatography. The yields of **2a**, **2g**, **2h**, and **2j** were determined by GC analysis based on the internal standard technique. ^{1}H and ^{13}C NMR spectra of isolated **2b**, **2c**, **2d**, **2e**, **2f**, and **2i** were good agreement with reported data.[13,16]

*5.2.1. 4-Methoxybenzaldehyde (**2b**):*
Pale yellow oil (57 mg, 83%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.85-7.83 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H).

*5.2.2. 4-Trifluoromethylbenzaldehyde (**2c**):*
Pale yellow oil (45 mg, 52%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H).

*5.2.3. 3-Pyridinecarboaldehyde (**2d**):*
Colorless solid (42 mg, 75%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 9.11 (s, 1H), 8.87-8.85(m, 1H), 8.21-8.17(m, 1H), 7.53-7.50 (m, 1H).

*5.2.4. 3-Phenyl-1-propanal (**2e**):*
Pale yellow oil (51 mg, 76%), ^{1}H NMR (400 MHz, $CDCl_3$): δ9.82 (s, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 8.0 Hz, 3H), 2.96 (t, J = 8.0 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H).

*5.2.5. 3-(4-Chlorophenyl)-1-propanal (**2f**):*
Pale yellow oil (119 mg, 70%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (m, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 2.78-2.74 (m, 2H).

*5.2.6. Tetradecanal (**2i**):*
White solid (90 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, J = 1.4 Hz, 1H), 2.42 (td, J = 7.6, 2.0 Hz, 2H), 1.66-1.59 (m, 2H), 1.34-1.23 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H).

5.3. General procedure for the palladium-catalyzed formal hydroacylation of allenes (Table 3 and Table 4)
To a 10 mL Schlenk flask with a magnetic stir bar, a carboxylic anhydride (**1**, 0.50 mmol), $PdCl_2(MeCN)_2$ (0.025 mmol, 5.0 mol %) were added. The flask was evacuated and backfilled with argon three times. Then, MeCN (1.0 mL) and an allene (**3**, 1.0 mmol) were added to the flask and the resultant solution was stirred at room temperature for 10 min. After tri-isopropylsilane (0.65 mmol) was added, the reaction mixture was stirred at 50 °C for 20 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, the products were isolated either by silica gel column chromatography or MPLC. ^{1}H and ^{13}C NMR spectra of isolated **4a**–**d** were good agreement with reported data.[6]

*5.3.1. (E)-3-Cyclohexyl-2-methyl-1-phenylprop-2-en-1-one (**4a**):*
Colorless oil (81 mg, 71%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dt, J = 6.8, 1.4 Hz, 2H), 7.48 (tt, J = 7.5, 1.4 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 6.11 (dd, J = 9.5, 1.4 Hz, 1H), 2.46 (tdt, J = 10.9, 9.5, 3.6 Hz, 1H), 1.98 (d, J = 1.4 Hz, 3H), 1.77-1.63 (m, 5H), 1.39-1.04 (m, 5H).

*5.3.2. (E)-3-Cyclohexyl-2-methyl-1-[4-(trifluoromethyl)phenyl]prop-2-en-1-one (**4b**):*
Pale yellow oil (121 mg, 81%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.64 (m, 4H), 6.10 (dd, J = 9.5, 1.4 Hz, 1H), 2.48 (tdt, J = 11.1, 9.5, 3.4 Hz, 1H), 1.99 (d, J = 1.4 Hz, 3H), 1.79-1.64 (m, 5H), 1.41-1.02 (m, 5H).

*5.3.3. (E)-3-Cyclohexyl-1-(4-methoxyphenyl)-2-methylprop-2-en-1-one (**4c**):*
Pale yellow oil (54 mg, 41%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dt, J = 9.2, 2.5 Hz, 2H), 6.91 (dt, J = 9.4, 2.5 Hz, 2H), 6.04 (dd, J = 9.5, 1.4 Hz, 1H), 3.86 (s, 3H), 2.45 (tdt, J = 11.1, 9.5, 3.6 Hz, 1H), 1.96 (d, J = 1.4 Hz, 3H), 1.78-1.62 (m, 5H), 1.40-1.04 (m, 5H).

*5.3.4. (E)-1-Cyclohexyl-2-methyl-5-phenylpent-1-en-3-one (**4d**):*
Pale yellow oil (105 mg, 81%), ^{1}H NMR ($CDCl_3$): δ 7.31-7.25 (m, 2H), 7.22-7.16 (m, 3H), 6.39 (dd, J = 9.1, 1.4 Hz, 1H), 3.00-2.89 (m, 4H), 2.36 (tdt, J = 11.1, 9.5, 3.8 Hz, 1H), 1.79 (d, J = 1.4 Hz, 3H), 1.77-1.61 (m, 5H), 1.37-1.01 (m, 5H).

*5.3.5. (E)-2-Methyl-1,5-diphenylhept-2-en-1-one (**4e**):*
Colorless oil (51 mg, 40%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dt, J = 8.1, 1.1 Hz, 2H), 7.47 (tt, J = 7.2, 1.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.23-7.15 (m, 3H), 6.28 (tq, J = 7.2, 1.4 Hz, 1H), 2.75 (t, J = 7.5 Hz, 2H), 2.60 (td, J = 7.5, 7.2 Hz, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 145.0, 141.0, 138.5, 136.9, 131.3, 129.2, 128.4, 128.3, 127.9, 126.1, 34.6, 30.7, 12.4. HRMS (m/z): $[M+H]^+$ calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1360.

*5.3.6. 2-Cyclohexylidene-1-phenylpropan-1-one (**4f**):*
Colorless oil (73 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dt, J = 6.6, 1.6 Hz, 2H), 7.54 (tt, J = 7.2, 1.6 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 2.30 (t, J = 6.1 Hz, 2H), 1.98 (t, J = 5.7 Hz, 2H), 1.87 (s, 3H), 1.69-1.62 (m, 2H), 1.59-1.52 (m, 2H), 1.47-1.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 140.2, 136.9, 133.0, 129.3, 128.6, 126.2, 32.8, 29.9, 27.7, 27.6, 26.4, 15.7. HRMS (m/z): $[M+H]^+$ calcd for for $C_{15}H_{18}O$: 214.1358. Found: 214.1358.

Acknowledgments

This work was supported by Grant-in-Aid for Scientific Research (A) and also by Grant-in-Aid for Scientific Research on Innovative Areas ("Molecular activation directed toward straightforward synthesis") from MEXT, Japan.

References and notes

1. For reviews, see: (a) Willis, M. C. *Chem. Rev.* **2010**, *110*, 725–748. (b) Leung, J. C.; Krische, M. J.; *Chem. Sci.* **2012**, *3*, 2202–2209. (c) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222–234. (d) Jun, C.-H.; Jo, E.-A.; Park, J.-W. *Eur. J. Org. Chem.* **2007**, 1869–1881. (e) Fu, G. C.; In *Modern Rhodium-Catalyzed Organic Reactions*, Evans. A. ed.; Wiley-VCH: Weinheim, **2005**; pp. 79–91.
2. Selected examples for intramolecular hydroacylations, see: (a) Hoshimoto, Y.; Hayashi, Y.; Suzuki, H.; Ohashi, M.; Ogoshi, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 10812–10815. (b) Coulter, M. M.; Dornan, P. K.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 6932–6933. (b) Kundu, K.; McCullagh, J. V.; Morehead, Jr. A. T. *J. Am. Chem. Soc.* **2005**, *127*, 16042–16043. (c) Sato, Y.; Ohnishi, Y.; Mori, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 1218–1221. (d) Tanaka, K.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 8078–8079. (e) Tanaka, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 11492–11493 (f) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190–197.
3. Selected examples for chelation-assisted hydroacylations, see: (a) von Delius, M.; Le, C. M.; Dong, V. M. *J. Am. Chem. Soc.* **2012**, *134*, 15022–15032. (b) Coulter, M. M.; Kou, K. G. M.; Galligan, B.; Dong, V. M. *J. Am. Chem. Soc.* **2010**, *132*, 16330−16333. (c) Murphy, S. K.; Petrone, D. A.; Coulter, M. M.; Dong, V. M. *Org. Lett.* **2011**, *13*, 6216−6219. (d) Zhang, H.-J.; Bolm, C. *Org. Lett.*

2011, *13*, 3900−3903. (e) Chaplin, A. B.; Hooper, J. F.; Weller, A. S.; Wills, M. C. *J. Am. Chem. Soc.* **2012**, *134*, 4885–4897. (f) Moxham, G. L.; Randell-Sly, H. E.; Brayshaw, S. K.; Weller, A. S.; Willis, M. C. *Chem.-Eur. J.* **2008**, *14*, 8383−8397. (g) Osborne, J. D.; Willis, M. C. *Chem. Commun.* **2008**, 5025−5027. (h) Moxham, G. L.; Randell-Sly, H. E.; Brayshaw, S. K.; Woodward, R. L.; Weller, A. S.; Willis, M. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7618−7622. (i) Jun, C.-H.; Lee, H.; Hong, J.-B. *J. Org. Chem.* **1997**, *62*, 1200–1201. (j) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 4564–4565; (k) Murphy, S. K.; Bruch, A.; Dong, V. M. *Angew. Chem. Int. Ed.* **2014**, *53*, 2455–2459.

4. (a) Kondo, T.; Akazome, M.; Tsuji, Y.; Watanabe, Y. *J. Org. Chem.* **1990**, *55*, 1286–1291. (b) Kondo, T.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 6229–6230.
5. Selected examples for oxidative and reductive formal hydroacylations, see: (a) Han, S. B.; Kim, I.-S.; Han, H.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 6916–6917. (b) Bower, J.; Skucas, E.; Patman, R. L.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 15134–15135. (c) Skucas, E.; Bower, J.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 12678–12679. (d) Shibahara, F.; Bower, J. F.; Krische, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 14120–14122. (e) Shibahara, F.; Bower, J. F.; Krische, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6338–6339. (f) Patman, R. L.; Chaulagain, M. R.; Williams, V. M.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 2066–2067. (g) Omura, S.; Fukuyama, T.; Horiguchi, J.; Murakami, Y.; Ryu, I. *J. Am. Chem. Soc.* **2008**, *130*, 14094–14095. (h) Hatanaka, S.; Obora, Y.; Ishii, Y. *Chem.-Eur. J.* **2010**, *16*, 1883–1888.
6. Fujihara, T.; Tatsumi, K.; Terao, J.; Tsuji, Y. *Org. Lett.* **2013**, *15*, 2286–2289.
7. (a) Gooßen, L. J.; Rodoríguez, N.; Gooßen, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 3100–3120.
8. (a) Kakino, R.; Yasumi, S.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 137–148. (b) Gooßen, L. J.; Ghosh, K. *Chem. Commun.* **2001**, 2084–2085. (c) Gooßen, L. J.; Ghosh, K. d *Eur J. Org. Chem.* **2002**, 3254–3267.
9. (a) Bercot, E. A.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 10248–10249. (b) Wang, D.; Zhang, Z. *Org. Lett.* **2003**, *5*, 4645–4648.
10. (a) Hong, Y. T.; Barchuk, A.; Krische, M. J. *Angew. Chem. Int. Ed.* **2006**, *45*, 6885–6888. (b) Kokubo, K.; Miura, M.; Nomura, M. *Organometallics* **1995**, *14*, 4521–4524.
11. (a) Kokubo, K.; Matsumasa, K.; Nishinaka, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 303–311. (b) Osborne, J. D.; Randell-Sly, H. E.; Currie, G. S.; Cowley, A. R.; Willis, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 17232–17233.
12. Nagayama, K.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1803–1815.
13. Fujihara, T.; Cong, C.; Terao, J.; Tsuji, Y. *Adv. Synth. Catal.* **2013**, *355*, 3420–3424.
14. (a) Nagayama, K.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 367–368. (b) Nagayama, K.; Kawataka, F.; Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1999**, *74*, 573–580.
15. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals, 5th ed.*; Burrerworth-Heinemann: Oxford, U. K., **2003**.
16. Fujihara, T.; Cong, C.; Terao, J.; Tsuji, Y. *Synlett* **2012**, *23*, 2389–2392.

Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.